

High Pressure Far Infrared Spectra of Lawsonite

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Beamline(s): U2A

Introduction: Substantially more water is currently subducted into the Earth's mantle than is released volcanically. An active area of research in the Earth sciences is concerned with the transport and storage of this water. Hydrous minerals with stoichiometric water (OH^- and H_2O) are common constituents of metamorphosed basalt, and are the phases that transport water into the mantle as part of the process of subduction. To understand the mantle's water budget it is important to know the thermodynamic properties of subduction zone minerals. These data include the heat capacity, thermal expansion, bulk modulus and Grüneisen parameters. As part of our ongoing effort to determine these thermodynamic parameters for common minerals in metabasalt we have recently used the U2A infrared beamline at NSLS to collect *in situ* far infrared (FIR) measurements of $\text{CaAl}_2\text{Si}_2\text{OH}_2(\text{H}_2\text{O})$ -lawsonite at high pressures.

Methods and Materials: For our high-pressure measurements we utilized a diamond anvil cell (DAC) and the synchrotron infrared radiation source to obtain high-quality spectra in a time frame that allowed data collection at many pressure points. The NSLS synchrotron source is coupled to a Bruker FTIR with a custom-built Ar-purged sample chamber. We used the same natural lawsonite sample that was used in a previous mid infrared (MIR) study (Scott and Williams 1999). Samples were prepared as a thin film by pressing a powdered sample between the diamond anvils. Petroleum jelly, which does not absorb in the FIR, was used as a pressure-transmitting medium, and the ruby fluorescence technique was used to measure pressure in all experiments.

Results: Ambient pressure FIR and MIR spectra of our sample are in good agreement with previous studies (e.g. Le-Cleac'h, A. and Gillet 1990). Our FIR spectra at selected pressures on compression and decompression are shown in Figure 1. We observe FIR absorption features at the following frequencies: 95, 170, 210, 320, 405, 420 and 480 cm^{-1} . With pressure we observe gradual changes in intensity, particularly in the mode initially at 405 cm^{-1} . With decompression all modes follow the frequencies on the compressive cycle although there is some hysteresis; however, the ambient-pressure, post-compression spectrum is identical to the pre-compression spectrum. Until approximately 8 GPa all modes increase monotonically with pressure.

Previous high-pressure spectroscopic and x-ray diffraction studies have observed a room temperature, fully reversible, phase transition (involving the symmetry of the OH^- groups) at 8.6 GPa (Scott and Williams 1999, Daniel et al 2000). This transition is manifested in the spectroscopic data by changes in slope of the mode frequencies with pressure (dv/dP), and has been interpreted to not involve significant changes in the aluminosilicate framework. Our primary motivation for the current FIR measurements was to check for the onset of this transition in low-frequency vibrations. As with the MIR and Raman data we observe changes in dv/dP near the pressure of the phase transition; we also observe the appearance of modes near 360 and 220 cm^{-1} at approximately 9.5 GPa.

We have combined our current results with existing data and calculated mode Grüneisen parameters ($\gamma_i = -\text{dlnv}/\text{dlnV}$) for all available data using several assumptions regarding the value of q ($q = \text{dln}\gamma/\text{dlnV}$); typically q is found to be between zero and two. Using the equation of state from Daniel et al (1999) ($K_{0T} = 124.1\text{ GPa}$, $\text{dK}/\text{dP} = 4$) we find an unweighted average Grüneisen parameter of ~ 0.84 (for $q=0$, $\gamma=0.81$ and for $q=2$, $\gamma=0.86$). By considering each mode's contribution to the heat capacity (C), and treating each mode as an Einstein oscillator ($C_{vi} = \kappa (h\nu_i/\kappa T)^2 \exp(h\nu_i/\kappa T) / (\exp(h\nu_i/\kappa T) - 1)^2$, where h and κ are the Planck and Boltzmann constants) we calculate a weighted average ($(\sum C_{vi}\gamma_i)/\sum C_{vi}$) and find a value of ~ 1.17 (for $q=0$, $\gamma=1.13$ and for $q=2$, $\gamma=1.20$). These values are almost 20% below the value we determine for the thermodynamic Grüneisen parameter ($\gamma_T = \alpha K/\rho C_p$): 1.44, and indicate that anharmonic contributions to the thermal expansion and heat capacity will be important.

Conclusions: We reached a maximum pressure of greater than 25 GPa (this pressure corresponds to a depth of approximately 750 km); previous phase equilibria experiments determined high pressure and temperature stability of $\sim 11\text{ GPa}$ at 800°C (Pawley 1994). This observation is important because it demonstrates the potential metastability in cold subduction zones for this phase.

References:

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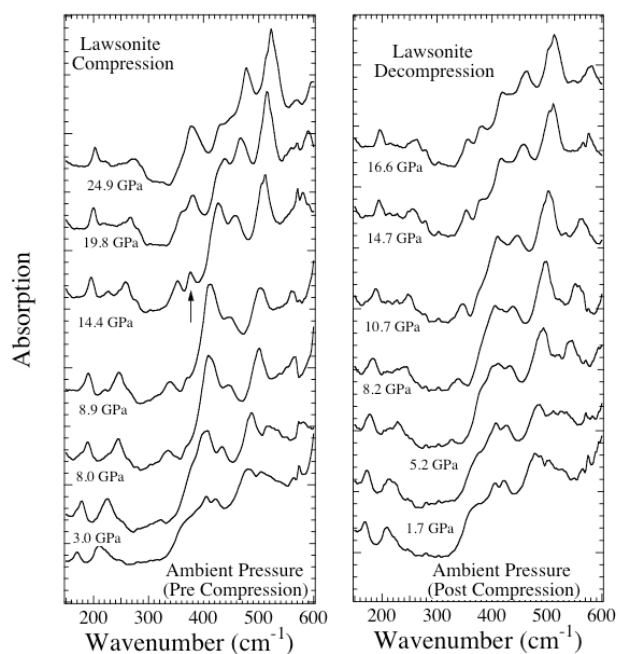


Figure 1 FIR compression and decompression spectra of lawsonite as a function of pressure to 25 GPa. Changes occur in the spectrum near 8 GPa, but are fully reversible upon decompression.